


Please type a plus sign (+) inside this box → [+]

PTO/SB/05 (1/98)
Approved for use through 09/30/2000. OMB 0651-0032
Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

 02/18/99 JCS549 U.S. PTO	UTILITY PATENT APPLICATION TRANSMITTAL		Attorney Docket No. 120194-4220A (124784A U.S.)	
	First Inventor or Application Identifier		Villarreal-Trevino, Juan A.	
	Title	METHOD AND APPARATUS FOR PRODUCING DIRECT REDUCED IRON WITH IMPROVED REDUCING GAS UTILIZATION		
	Express Mail Label No.		EL228912087US	

APPLICATION ELEMENTS See MPEP chapter 600 concerning utility patent application contents.	ADDRESS TO: Assistant Commissioner for Patents Box Patent Application Washington, DC 20231
--	--

1. ☒ * Fee Transmittal Form (e.g., PTO/SB/17)
(Submit an original, and a duplicate for fee processing)
2. ☒ Specification [Total Pages 32]

(preferred arrangement set forth below, MPEP 1503.01)

- Descriptive title of the Invention
- Cross References to Related Applications
- Statement Regarding Fed sponsored R & D
- Reference to Microfiche Appendix
- Background of the Invention
- Brief Summary of the Invention
- Brief Description of the Drawings (if filed)
- Detailed Description,
- Claim(s)
- Abstract of the Disclosure

- ☒ Drawing(s) (37 CFR. § 1.152) [Total Sheets 6]

Oath or Declaration [Total Pages 2]

- a. ☒ unsigned
- b. ☐ Copy from a prior application (37 C.F.R. § 1.63(d))
(for continuation/divisional with Box 17 completed)
[Note Box 5 below]

- i. ☐ **DELETION OF INVENTOR(S)**
Signed statement attached deleting
inventor(s) named in the prior application,
see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).

- ☐ Incorporation By Reference (useable if Box 4b is checked)
The entire disclosure of the prior application, from which a
Copy of the oath or declaration is supplied under Box 4b, is
Considered to be part of the disclosure of the accompanying
Application and is hereby incorporated by reference therein.

6. ☐ Microfiche Computer Program (Appendix)
7. Nucleotide and/or Amino Acid Sequence Submission
(if applicable, all necessary)
- a. ☐ Computer Readable Copy
 - b. ☐ Paper Copy (identical to computer copy)
 - c. ☐ Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

8. ☐ Assignment Papers (cover sheet & documents(s))
9. ☐ 37 C.F.R. § 3.73(b) Statement ☐ Power of Attorney
(when there is an assignee)
10. ☐ English Translation Document (if applicable)
11. ☐ Information Disclosure Statement (IDS)/PTO-1449 ☐ Copies of IDS Citations
12. ☐ Preliminary Amendment
13. ☒ Return Receipt Postcard (MPEP 503)
(Should be specifically itemized)
14. ☐ * Small Entity ☐ Statement filed in prior application,
Statements(s) Status still proper and desired
(PTO/SB/09-12)
15. ☐ Certified Copy of Priority Document(s)
(if foreign priority is claimed)
16. ☐ Other: _____

* A new statement is required to be entitled to pay small entity fees, except where one has been filed in a prior application and is being relied upon.

17. If a **CONTINUING APPLICATION**, check appropriate box, and supply the requisite information below and in a preliminary amendment:

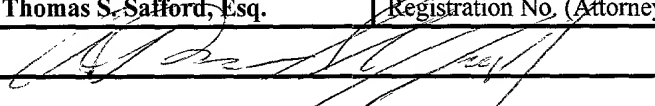
☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No.:

Prior application information: Examiner _____ Group/Art Unit: _____

16. CORRESPONDENCE ADDRESS

☐ Customer Number or Bar Code Label or ☐ New correspondence address below
(Insert Customer No. or Attach bar code label here)

Name	A. Thomas S. Safford, Esq. FROMMER LAWRENCE & HAUG LLP				
Address	745 Fifth Avenue				
City	New York	State	NY	Zip Code	10151
Country	U.S.	Telephone	(212) 588-0800	Fax	(212) 588-0500

Name (Print/Type)	A. Thomas S. Safford, Esq.	Registration No. (Attorney/Agent)	21,002
Signature			Date February 18, 1999

Burden Hour Statement: This form is estimated to take 0.2 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Box Patent Application, Washington, DC 20231

DA0210

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION FOR LETTERS PATENT

Title : METHOD AND APPARATUS FOR PRODUCING DIRECT REDUCED
IRON WITH IMPROVED REDUCING GAS UTILIZATION

Inventors : Juan Antonio Villarreal-Treviño

EXPRESS MAIL

Mailing Label Number: EL228912087US

Date of Deposit: February 18, 1999

I hereby certify that this paper or fee is being
deposited with the United States Postal Service
"Express Mail Post Office to Addressee" Service
under 37 CFR 1.10 on the date indicated above and
is addressed to the Assistant Commissioner for Patents
Washington, D.C. 20231

Howard Cutler

(Typed or printed name of person mailing paper or fee)

Howard Cutler

(Signature of person mailing paper or fee)

A. Thomas S. Safford
Registration No. 21,002
Edgar H. Haug
Registration No. 29,309
FROMMER LAWRENCE & HAUG LLP
Attorneys for Applicants
745 Fifth Avenue
New York, New York 10151
TEL: 212-588-0800
FAX: 212-588-0500
Attorney Docket No.:
120194-4220A (124784A U.S.)

RELATED APPLICATIONS

This is a continuation-in-part of copending provisional application serial number 60/075,313, filed February 20, 1998.

FIELD OF THE INVENTION

5 The present invention relates to a method and apparatus for the production of prereduced iron ore, Direct Reduced Iron (DRI), or the like, in an reduction system comprising a reduction reactor, a source of natural gas, which is transformed in the operation of said system by means of a reformer and/or by the catalytic action of the metallic iron within said reduction reactor, to a reducing gas having carbon monoxide and hydrogen as its main constituents, and a heating device for heating said reducing gas prior to its introduction into the reduction zone of said reduction reactor. More particularly the invention relates to a method and apparatus which allows for a higher utilization of the chemical reduction potential of the reducing gas in the reduction system with a corresponding increase in the productivity of said reduction reactor or a decrease in the make-up quantity of gas needed for a given production level. This invention provides
10
15
20 a way for increasing productivity of existing reduction systems at lesser investment and operational costs as compared with the conventional alternatives of increasing the capacity of the reducing gas generator or of the known measure of installing a carbon dioxide removal system in the recycle stream of reducing
25 gas.

BACKGROUND OF THE INVENTION

Direct reduction plants for producing direct reduced iron, known as DRI or sponge iron, hot briquetted iron, or the like (in general prereduced materials useful as feedstock for iron and steelmaking), currently produce such materials by contacting a reducing gas, composed principally of hydrogen and carbon monoxide, at temperatures in the range from 750°C to 1050°C, with a bed of particulate iron-containing material in the form of lumps, pellets or mixtures thereof. The bed of iron-containing material may be static or may be descending by gravity within a reduction reactor. Examples of such processes are described in U.S. patent Nos. 3,749,386; 3,764,123; 3,816,101; 4,336,063; 4,428,072; 4,556,417; 5,078,787; 4,046,557; 4,002,422 and 4,375,983.

It is well known that in direct reduction systems the reducing gas and the oxides being reduced reach an equilibrium which does not allow the full utilization of the reducing gas in the reduction reactor. Consequently, for efficiency the currently operating plants recycle regenerated reducing gas in order to minimize the need of make-up reducing gas. However, there has always been the need to purge or otherwise eliminate a significant portion of the spent reducing gas available to be recycled to prevent accumulation of carbon dioxide and inert elements (such as N₂) in the system. The portion of gas purged normally is utilized as fuel in the reformer or gas heater of the system. This utilization as fuel recovers only the heating value of the purged

reducing gas but not the chemical value of its costly hydrogen and carbon monoxide. If most of the chemical value, instead of being purged, could rather be utilized for reduction of iron oxides, then the amount of make up gas needed for a given level of production would be lowered, or alternatively the production would be increased for the same reformer capacity. Regeneration to upgrade the spent reducing gas effluent from the reduction reactor involves elimination of the reduction reaction products i.e. carbon dioxide and water which come out of the reduction reactor in the amounts determined by the chemical equilibrium of these products from the residual hydrogen, carbon monoxide, methane (and any other higher hydrocarbons present in minor amounts in the reducing gas).

It has long been known from a number of prior art references, for example U.S. Patent No.2,547,685 to Brassert et al; U.S. Patent No. 4,584,016 to Becerra-Novoa et al.; U.S. Patent No.4,001,010 to Kanbara et al.; U.S. Patent No.4,129,281 to Ono et al.; U.S. Patent No. 3,853,538 to Nemeth et al.; and U.S. Patent 4,046,557 to Beggs, to remove water and carbon dioxide from the reducing gas stream which is to be recycled to the reduction reactor. Water is conventionally removed by quench cooling. For CO₂ removal, all these patents, however, teach the utilization of a CO₂ removal unit, usually of the type where the CO₂-containing gas is contacted with a liquid solution which reacts with said CO₂, and treats the recycle gas as a whole.

These chemical absorption systems have to be provided with some source of heating, normally in the form of steam, for regenerating the solution, which requirement is costly and in some applications is not readily available. The energy needed for
5 regeneration of the CO₂ absorbent solution, and the capital costs for these CO₂ removal units of large capacity are high.

This is to be compared with the CO₂ removal units of the so-called Pressure Swing Adsorption (PSA) and Vacuum Pressure Swing Adsorption (VPSA) systems, which are most preferably used according to the present invention.

The PSA type gas separation systems have also long been known. Exemplary patents are U.S. patents Nos. 3,788,037;
4,869,894; 4,614,525; 5,026,406 and 5,152,975. See also 5,833,734
and 5,858,057. These and the other patents cited herein and their
15 content are incorporated by reference.

OBJECTS AND SUMMARY OF THE INVENTION

In the prior art of the direct reduction processes, there is no teaching or suggestion to recover H₂ (and/or CO) from the gas purge, and especially there is no such teaching to do so
20 by using physical adsorption systems of the PSA type for CO₂/H₂ separation. Such PSA systems rely not on a chemical reaction with CO₂, but rather on activated surfaces that are selective for adsorption of specific component(s) from the gas stream. In the present invention, the PSA systems preferably used, function by
25 adsorption of the larger molecules, particularly CO₂, while

passing mainly only the lighter H_2 . Because of physical similarities, most of the CO is removed with CO_2 and the heavier molecules. Perhaps because the PSA system separates desirable CO together with the unwanted CO_2 from the H_2 , thus the PSA use seems counter-intuitive. Nevertheless, the applicant has determined that PSA use overall has several distinct advantages over the more costly prior CO_2 solution absorption systems. The use of a PSA system results in recycling more hydrogen to the reactor by treating only the purged gas and recovering therefrom the hydrogen values of such purged gas by utilization of a PSA CO_2 removal unit.

This specific inventive concept also has the advantage that the unit treats a smaller amount of gas and therefore the capital costs are less, and also the regeneration of the adsorbent is made by pressure changes and not by heating (thereby requiring less energy to run). This type of gas separation produces a gas stream from the PSA unit which is rich in hydrogen, with a hydrogen content higher than 92% of the volume, which is advantageously recycled to the reactor system and used as part of the reducing gas.

The present invention thus involves recycling a first portion of the gas effluent from the reduction reactor back to said reactor and simultaneously separating for recycle a hydrogen rich gas stream from a purged second portion of said effluent gas. The separation from each other of the H_2 and CO_2 content of the

purged portion of the effluent gas in the broadest aspects of the invention can be by any separation means (including absorption) but most preferably is by PSA adsorption. The ratio of said second portion to said first portion can vary widely (including
5 from less than 1:4 to more than 1:1).

In other words, the present invention is based on the principle of separating hydrogen from the portion of reducing gas which is normally removed from the reactor system as a purge (whose only past use typically has been as a high priced source of a relatively low grade fuel). The invention thus distinguishes
10 from the prior art in that hydrogen and carbon monoxide recycling to the reduction reactor is effected in two ways: one is a direct recycling of a portion of the effluent gas and the other is a recycling of a gas stream highly rich hydrogen obtained by the separation of CO₂ (and necessarily CO too, when using the
15 preferred PSA separation system) from the gas stream which is normally purged and used as fuel. By the present invention, hydrogen is recuperated and used as chemical reductant instead of only burning it as fuel.

20 It is therefore an object of the present invention to provide a method and an apparatus for producing direct reduced iron in a reduction system where quality of the recycle gas is enhanced by a more effective removal of reaction products from the recycle gas and an increase in the amount of hydrogen recycled to
25 the reactor.

It is a further object of the present invention to provide a method and an apparatus for producing direct reduced iron in a reduction system where the productivity of said system is increased by an enhanced recycling to include hydrogen
5 separated from the purged reducing gas (which formerly was entirely purged without recycling any useful portion thereof).

It is another object of the invention to provide a method and apparatus for either or both increasing the productivity of a direct reduction system and/or decreasing the capital investment and operational costs related to the necessary upgrading of the spent recycle gas.

Other objects and advantages of the invention will be evident to those skilled in the art or will be described in this specification of the invention and the appended drawings.

According to the present invention, the objects thereof are achieved by providing a method and apparatus by the following preferred embodiment:

A method for producing DRI which comprises feeding a reducing gas mainly composed of hydrogen and carbon monoxide and also comprising methane, carbon dioxide and water, heated at a
20 temperature between about 850°C to about 1050°C, to a reduction reactor wherein solid particles within said reactor containing iron oxides are reduced largely to sponge iron by reaction of said iron oxides with said reducing gas; withdrawing as top gas from
25 said reactor said reducing gas after reacting with said iron

oxides; cooling and cleaning said top gas and removing water therefrom; recycling a first portion of said top gas to said reduction reactor; removing at least CO₂, preferably by a PSA or VPSA adsorption unit from a second portion of said top gas to form
5 a hydrogen rich gas stream (with a hydrogen content preferably higher or equal to 92% by volume, and most typically higher than 95% by volume) and a hydrogen lean gas stream (usually containing mainly CO₂, CO, some CH₄, and residual H₂); and recycling said hydrogen rich gas stream to said reduction reactor.

The objects of the invention are also achieved by providing an apparatus for producing DRI which comprises a reduction reactor having a reduction zone with a gas inlet and a gas outlet; a gas cooler in fluid communication with the gas outlet of said reduction zone; a reducing gas heater in fluid communication with the gas inlet of said reduction zone; first
10 pumping device connected to said cooler and to said heater to recycle reducing gas from said gas outlet to said gas inlet; conduit for diverting a portion of the reducing gas effluent derived from said gas outlet of said reduction zone to a second
15 pumping device; a CO and CO₂ PSA or VPSA adsorption unit for separating CO and CO₂ from a gas stream; and conduit communicating said second pumping device to said CO and CO₂ PSA or VPSA
20 adsorption unit; and conduit to communicate said CO and CO₂ PSA or VPSA adsorption unit with separating with the gas inlet of said
25 reduction zone.

BRIEF DESCRIPTION OF THE DRAWINGS

In this specification and in the accompanying drawings, some preferred embodiments of the invention are shown and described and various alternatives and modifications thereof have been suggested; but it is to be understood that these are not intended to be exhaustive and that many other changes and modifications can be made within the scope of the invention. The suggestions herein given are selected and included for purposes of illustration in order that others skilled in the art will more fully understand the invention and the principles thereof and will thus be enabled to modify it in a variety of forms, each as may be best suited to the conditions of a particular use.

In each of the following figures, there is illustrated a PSA unit for treating the gas purged from the spent dewatered recycle gas for recovering and returning the H_2 component of the purge to the reactor.

Figure 1 shows schematically one of the preferred embodiments of the present invention, illustrated by a diagram of a moving bed process for producing DRI where the source of the H_2 and CO makeup reducing gas is a conventional "off line" steam/natural gas reformer, and the recovered purged H_2 is mixed back with the recycle gas fed through the heater and on to the reactor.

Figure 2 shows schematically another embodiment of the invention where the reducing gas is produced within a "self-reforming" reduction system by a natural gas reformation within

said system (where no reformer is needed and the added natural gas make up by reaction with oxidants H_2O and CO_2 is transformed into hydrogen and carbon monoxide within said system, particularly within the reduction reactor by the catalytic action of the reduced iron present in said reactor), and the H_2 recovered from purge gas is returned to the heater in a manner similar to Figure 1.

Figure 3 shows schematically a further embodiment of the invention plus three additional illustrative alternative variations (shown in dotted lines), where the reducing gas is produced in a CO_2 -natural gas "in line" reformer and added make up natural gas is combined in the reformer with the existing oxidants H_2O and CO_2 present in the recycle reducing gas. In the variations of this embodiment, the hydrogen recuperated by the PSA unit for recycle to the reduction zone of the reactor can be 1) fed to the reformer for heating (if the latter is of sufficient capacity), 2) heated in a separate heater (by-passing the reformer, useful in avoiding need to modify a reformer when upgrading an existing plant installation), 3) fed to the outlet from the reformer (relying on an oxygen-fed partial combustion for heating, reducing the size and cost of the reformer), or 4) fed to the cooling gas inlet of the reduction reactor (relying on a heat exchange with the hot DRI descending in the cooling zone of the reactor, while at least partially flowing upwardly into the reduction zone). The cooling loop shown in any of these drawings

can be omitted for those installations where the DRI is to be discharged hot for briquetting or hot charging directly to an EAF.

Figure 4 shows schematically an embodiment similar to that in Figure 2 with the difference that the natural gas feed to the reducing gas loop may be optional and there is at least a partial natural gas feed to the cooling zone, preferably with a cooling gas loop and/or a gas flow link from the cooling gas outlet to the reducing gas loop (depending on how various valves, illustrated or not, are set). In the embodiment and variations in this and the following figures the natural gas which is fed to the cooling zone cracks the methane and other hydrocarbons when contacting the hot descending DRI, allowing the deposition of carbon on the DRI and also resulting in a lighter hydrocarbons, CO, and H₂ gases for use in the reducing zone.

Figure 5 shows schematically an embodiment similar to that in Figure 4 with the difference that some recycled cooling gas is diverted and heated in a separate heater and feed to the recycle reducing gas at the inlet to the reduction zone.

Figure 6 shows schematically an embodiment similar to that in Figure 3 with the difference that natural gas is fed also to the cooling gas loop.

By such introduction of natural gas into the lower part of said reduction reactor as shown in figures 4-6, the resulting cooling gas stream is heated by its contact with the hot DRI within the cooling zone of the reactor and at least a significant

portion of this gas is allowed to travel upwardly within said reactor to the reduction zone. See U.S. Patent 4,556,417.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The invention is herein described as applied to direct
5 reduction systems having moving bed reactors, but it will be understood that it can be adapted to plants having fixed bed or fluidized bed reactors. With reference to Figure 1, numeral 10 generally designates a reduction reactor having a reduction zone 12 and a discharge zone 14. Solid particles containing iron
10 oxides 16, for example iron ore in the form of pellets or lumps, are fed to the upper portion of the reduction zone 12 and flow downwardly through said reactor 10 where iron oxides are at least partially reduced to metallic iron and are finally withdrawn typically as DRI from the reactor 10 through the discharge zone 14
15 as indicated by arrow 18. A stream of hot reducing gas 20 is fed to the lower part of the reduction zone 12 comprising reductants like hydrogen and carbon monoxide as well as some oxidants like water and carbon dioxide resulting from the reduction reactions of said iron oxides and is caused to flow upwardly countercurrent to
20 the descending solid particles. The reducing gas exits the reduction zone 12 at its upper part as top gas stream 22, which is cooled down with quenching water in a direct contact cooler 24. This cooling and washing with water cleans the top gas 22 of entrained dust and also condenses and separates the water produced
25 by the reduction reactions. The resulting clean and cool top gas

stream 26 is split into a dewatered recycle gas stream 28 and a purge gas stream 30.

The gas stream 28 is moved by a pumping device 32, which may be a blower or a compressor depending on the operating pressure of the reduction system, and is directed to a gas heater 34 before being recycled as gas stream 20 into the reduction zone 12.

Natural gas (and/or other reformable hydrocarbons) 36 and steam 38 are fed to a conventional gas-steam reformer 40 to yield hydrogen and carbon monoxide in a manner known in the art, producing a hot gas stream of reducing gas 42 which is cooled down in cooler 44 and results in a make-up reducing gas stream 46 of high reduction power. This make-up gas stream 46 is added to dewatered recycle stream 28, producing an improved cool reducing gas 48, chemically suitable for efficient reduction of iron oxides.

The other portion of cool top gas 26, namely stream 30, which in the prior art systems is a purge gas normally flared or used only unmodified as fuel in the reformer and gas heater(s), is here passed through second pumping device 50 and then treated in a Pressure Swing Adsorber unit (PSA) or a Vacuum Pressure Swing Adsorber unit (VPSA) 52, (both of which for convenience will be referred to herein generally as PSA, unless clearly indicated in the context to be the species exclusive of VPSA). The PSA unit 52 utilizes adsorbent surfaces to adsorb large molecules, mostly

carbon monoxide and carbon dioxide from the gas stream 30 (which stream 30 additionally comprises methane, water and nitrogen), and produces a hydrogen rich stream 54 with a high volume% content of hydrogen of from about 92% to more than 99%, preferably higher than 95 volume%, and a lean stream 56 with a low volume% content of hydrogen on the order of 10% to 25% by volume. Stream 54 with the high hydrogen content comprises make-up gas which is combined with the recycled reducing gas stream 48 producing an enhanced reducing gas stream 58 with a content of hydrogen and carbon monoxide in volume% on a dry basis as follows:

H₂: 50% to 70%
CO: 10% to 17%.

The reduction potential and quality of the upgraded recycle gas stream 58 is higher as compared with the composition of reducing gas utilized in the prior art systems (even those using CO₂ solution absorption columns).

The temperature of the reducing gas stream 58 is raised in heater 34 to levels between about 750 to 1050°C, preferably from 900 to 950°C, suitable for efficient reduction of iron oxides. Oxygen or enriched air with oxygen 60 (having a content preferably higher than 30% in volume of oxygen) may be combined with the hot reducing gas 20 in order to obtain the higher temperatures at the reduction zone with a corresponding increase in productivity or in order to have the same productivity but requiring a lower duty in the gas heater. This productivity increase with higher temperatures is due to higher reaction rates

and also to transformation of hydrocarbons present in the reducing gas to H_2 and CO by the partial combustion of the reducing gas with oxygen.

The lean gas stream 56 still includes among its constituents carbon monoxide and some methane, as well as small amounts of other gaseous hydrocarbons, which have heating value and may be used as fuel to fire the gas heater 34. The energy in gas stream 56 however usually is insufficient to fulfill all the heating needs of heater 34, so unreformed natural gas or other lower cost suitable fuel 62 is added to supplement said stream 56 (to produce an effective fuel supply in line 64 for the heater 34).

The DRI or prereduced materials 18 produced in the reduction zone 12 may be discharged at high temperatures on the order of $400^{\circ}C$ to $750^{\circ}C$ and can be hot briquetted or pneumatically transported to steelmaking furnaces, for example electric arc furnaces, thus reducing the energy needs in such steelmaking operations. Optionally, the DRI is cooled down in the discharge zone 14 by contact of the hot DRI with a cooling gas stream 66 comprising natural gas, a portion of the reducing gas stream 30 or stream 56, or other suitable gas which does not reoxidize said DRI. The discharge zone cooling gas effluent 68 may be cooled down and recycled as stream 66 in a manner known in the art.

Referring now to Figure 2, where the same numerals are used here (and in all the other figures also) to designate the

same elements as in Figure 1, this embodiment of the invention illustrates the invention as incorporated in a reduction system where the reducing gas is not generated in a natural gas-steam reformer but is generated by reformation of natural gas by partial combustion of methane present in the reducing gas with oxygen and/or by methane cracking and reformation with oxidants present in the reduction zone by the catalytic action of the iron-bearing particles in said reduction zone. In this embodiment the steam reformer 40 is dispensed with and a make up stream of natural gas 36 is instead added directly to the recycled gas stream 28, which is then combined with the hydrogen rich stream 54 to produce a combined gas stream 58. The water content in the gas stream 58 is adjusted by addition of water/steam stream 67 so that the amount of water present is between 3% and 10% by volume, suitable to be sufficient to carry out such reformation of methane within the reduction zone. This water regulation may also be effected for example as described in U.S. Patent No. 5,110,350, where the water added at 67 is advantageously taken from the hot water effluent from gas cooler 24.

Figure 3 illustrates the invention as applied to a reduction system where the reducing gas is generated in a reformer 40A of the type where natural gas from source 36 is combined with recycled gas 28 from the reduction reactor and reacts in the presence of a catalyst with oxidants such as the CO_2 and H_2O present in said recycled gas. This is sometimes referred to as an

"in-line" reformer (as contrasted with the "off-line" reformer 40 of Figure 1; which latter reformer does not act on the recycled gas, being outside of the recycle gas loop). Examples of these "in-line" reduction systems are U.S. Patents Nos. 3,748,120 and 3,749,386. In these types of reduction systems, the reformer 40A also functions as a heater, being fed with a combination of relatively cool natural gas 36 and recycled gas 28, and the reducing gas produced exits the reformer at a temperature between 800°C and 950°C. In this embodiment, the temperature of the reducing gas may also be increased by an addition of a stream of oxygen or of air enriched with oxygen 60 in order to increase the productivity of the reduction reactor (at a small sacrifice in reducing potential of the gas 20). For existing operating reduction systems, the reformer 40A most probably does not have sufficient capacity for heating the additional amount of hydrogen rich gas stream and consequently as a supplement or alternative to O₂-addition a separate gas heater 34A fed by the hydrogen rich stream 54a can be provided for this purpose (which feeds the hot hydrogen rich stream through line 70 to line 20, preferably downstream of line 60).

Figure 3, as illustrated, includes a further variation where the hydrogen rich stream 54b is heated in the reformer 40A without the need of a separate heater, assuming that the reformer has sufficient heating capacity for heating the additional amount of hydrogen rich gas. Although it is preferred to provide the

additional heater 34A (because in this way the recycled hydrogen rich stream 54a does not need to pass through the catalyst beds in the reformer 40A), in certain existing conditions it may be more feasible to design new reduction systems without said separate
5 heater 34A.

Figure 3, illustrates yet another variation where the hydrogen rich stream 54c is introduced directly to the hot reducing gas stream 20 prior to its introduction to the reactor system without having been separately heated (thus saving the cost of a separate heater). Since the reformer 40A typically would not have sufficient capacity for heating the additional amount of hydrogen rich gas stream 54c, and the temperature of said stream 54c decreases the temperature of the reducing gas, the addition of the oxygen containing gas 60 is sufficient to increase the
10 temperature of the hot reducing gas stream 20 to the desired levels. In another case (depending on the properties of the ore to be processed), the temperature of the reducing gas stream 20 might be too high and could be decreased intentionally with stream 54 to avoid overheating and resultant sticking of the DRI within
15 the reactor.

Figure 3 also illustrates a fourth variation similar to the last, but wherein the hydrogen rich stream 54d is instead introduced to the lower part of the reduction reactor (cooling zone) by combination with the cooling gas stream 66. Even though
20 this embodiment of the invention is very useful, it does not take

full advantage of the reducing potential of the hydrogen contained is stream 54d, because likely only a relatively small portion of stream 54d could be used in the reduction zone.

Figure 4, similar to Figure 2, shows how the present invention can be applied to an existing "self reformer" type installation. In this embodiment, the natural gas feed 36 can be diminished in quantity and potentially even eliminated by use of an alternative natural gas feed 36A to the cooling zone. In Figure 4, a full cooling recycle loop is illustrated, including the inlet 66 and outlet 68 of the cooling gas stream, the quench cooler 39, and the compressor 41. The natural gas feed 36A is to the gas inlet 66. Figure 4 also includes a connection 43 from the cooling gas loop to the reducing gas loop which can function as an indirect makeup gas external feed to the reducing zone (which could completely replace the feed in line 36).

Depending upon how the valves 35 and 37 are set, this can take any of a number of configurations. Of course, if one particular configuration is preferred, then the valves, piping and cooling loop elements can be included or omitted as appropriate. Other variations not specifically illustrated could be made, such as having compressor 41 positioned immediately after quench cooler 39 so that line 43 could feed downstream of compressor 32, rather than upstream.

Among the illustrated variations, if valve 37 is closed and valve 35 open, then the compressor 41 would be inoperative and

not needed. In such case, all of the natural gas added would be fed in through line 36A, pass through the cooling zone 14 (where some would be used for adjusting the carbon content of the hot descending DRI, some would be endothermically partially reformed in the presence of such DRI, a portion could flow upwardly from the cooling zone 14 already partially heated by the hot descending DRI for further reformation and use for reduction in the reducing zone 12, with the remainder passing externally from the reactor through outlet 68, cleaned and quench cooled in quench 39, pass on through open valve 35 in connecting line 43 and ultimately be fed to the reducing gas recycle loop at line 28.

An alternative configuration would be with both valves 35 and 37 open for those installations where the once-through flow of natural gas in the cooling zone 14 is insufficient and therefore recycling in the cooling loop is required.

A further configuration of Figure 4 would be with both valves 35 and 37 closed. This would be the equivalent of having only natural gas from line 36A feed through line 66 into the cooling zone 14 (with no cooling recycle) with all of such natural gas flowing upwardly into the reduction zone 12. This would insufficiently cool the exiting DRI 18 for cool discharge and would be alternatively too much cooled for hot discharged for briquetting or charging to an electric art furnace, if all of the natural gas feed were completely through line 36A. Consequently, a balance between a feed through line 36A and line 36 would

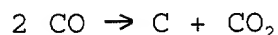
typically be made by appropriate adjustment to existing process conditions.

Figure 5 is very similar to Figure 4, but shows a further variation where line 43 connecting the cooling gas loop and the reducing gas loop instead of feeding into line 28 upstream of the compressor 32 and heater 34, instead feeds to line 20 downstream of the heater 34, thus requiring an auxiliary heater 34B (in those cases where the partial combustion of added oxygen at 60, would be insufficient or too disruptive of the gas composition fed in line 20 into the reducing zone).

The embodiment in Figure 6 is similar to the various embodiments illustrated in Figure 3 (wherein an "in line" reformer 40A is utilized) but further modified to have natural gas feed, preferably supplemental to feed 36, be to the cooling loop through line 36A.

Another advantage of the present invention results from the recycle stream having a higher content of hydrogen, which makes it possible to process a higher amount of gas due to the low heat capacity of hydrogen as compared to the heat capacity of the CO. This characteristic of hydrogen, allows one to process a larger amount of reducing gas through the gas heater or the reformer of a given size. Also, when one withdraws only CO₂ from the recycled gas stream 30 (as in most of the current prior art), the ratio between CO and CO₂ is increased to higher levels. That causes the gas to have a higher carburizing potential, which could

cause the metal dusting effect inside of the heater pipes or in the reformer pipes, due to the reaction:



Metal dusting a well known problem, which involves is an attack at process temperatures by carbon on the steel of the process equipment. With the present invention, the main component of the recycled stream is hydrogen, which avoids the metal dusting problems. It has been found that a ratio CO/CO₂ higher than 3 could cause carburizing problems in the thermal equipment, unless special alloys or inhibitors are used.

Another advantage of the invention that results from recycling mainly hydrogen, whose molecule is lighter than the CO, is in enabling a larger amount of recycle gas to pass through the reduction reactor and through the solid particles therein with a small increase in the pressure drop through said reactor and other equipment (such as the reformer or heater). With this advantage, the electric energy required by the compressor to circulate the reducing gas is decreased.

EXAMPLE

An example of the claimed process as calculated for potential implementation of an existing reduction system of the type illustrated in Figure 1 (but with a cooling gas loop and natural gas feed thereto, as in Figure 6). This is described as

follows. A reducing gas 46 produced in steam-natural gas reformer 40 has the following composition on a dry basis in volume %:

5 H₂: 50% to 60%
 CO: 30% to 37%
 CO₂: 2% to 3.5%
 CH₄: 1% to 3%
 N₂: 0% to 1.5%

with the rest being lesser amounts of other hydrocarbons and inert gases.

10 This gas is fed as make up to the reduction system as stream 46. About 50% of the top gas 26 from the reduction zone is diverted as stream 30, with a composition on a dry basis in volume % as follows:

15 H₂: 35% to 45%
 CO: 18% to 25%
 CO₂: 10% to 20%
 CH₄: 2% to 4%
 N₂: 0% to 3%.

20 This is compressed and passed through a PSA adsorption system 52. A gas stream 54 is obtained with a hydrogen content in volume% on a dry basis between of 92% and 99%. The recuperation of hydrogen from the gas stream 30 which is now used as chemical reductant instead of being used only as fuel, produces an increase in the rate of production of the reduction reactor in the best conditions
25 up to about 50%.

 From the foregoing description it should be apparent that the present invention provides a process capable of achieving the several objects of the invention set forth above. Thus it provides a novel and exceptionally efficient method of increasing

the production capacity of existing reduction systems by advantageously utilizing hydrogen which in the prior art is purged and burned as fuel, instead of taking advantage of its chemical reducing potential.

5 Depending on the composition of the reducing gas to be treated for recovering its hydrogen content, approximately 40% by volume of the overall effluent gas treated is recycled. The rest of the effluent gas is burned as fuel.

 As an example, if a reducing gas 30 has the following composition (by volume):

40
45
50
55
H₂: 55%;
CO: 21%;
CO₂: 15%;
CH₄: 6%;
N₂: 1%;
H₂O: 2%;

and is treated in a CO and CO₂ removal unit 52, the hydrogen rich stream 54 could contain: 95% to 100% by volume of H₂; and the hydrogen poor stream 56 would be composed of:

20
25
H₂: 25%;
CO: 35%;
CO₂: 26%;
CH₄: 11%;
N₂: 1%;
H₂O: 2%;

From this, it can be seen that more than 75% of the H₂ content of the purge stream in this example is recovered for recycle and essentially all of the CO₂ content thereof is permanently purged. In another example, if the hydrogen rich stream is 98% H₂, the

remaining 2% is CO, with only traces of other gases such as N₂ or CH₄.

It is of course to be understood that the foregoing description is intended to be illustrative only and that numerous
5 changes can be made in the structure of the system described and its operating conditions without departing from the spirit of the invention as defined in the appended claims.

120194-4220A (124784A U.S.)

WHAT IS CLAIMED IS:

1 1. A method for producing direct reduced iron DRI or
2 prereduced iron ore with improved reducing gas utilization,
3 comprising:
4 feeding a stream of reducing gas mainly composed of hydrogen
5 and carbon monoxide and also comprising methane, carbon dioxide
6 and water, heated at a temperature between about 750°C to about
7 1050°C, to a reduction zone within a reduction reactor wherein
8 solid particles containing iron oxides present therein are reduced
9 by reaction of said iron oxides with said reducing gas;
10 withdrawing from said reactor said reducing gas after
11 reacting with said iron oxides as top gas;
12 cooling and cleaning said top gas and removing water
13 therefrom to produce a cooled top gas;
14 heating and recycling a first portion of said cooled top gas
15 to said reduction reactor as part of said stream of reducing gas;
16 purging a second portion of said cooled top gas;
17 adding make-up gas to gases eventually recycled to the
18 reducing zone;
19 separating from said second portion of said cooled top gas at
20 least the majority of the hydrogen contained therein to form a
21 hydrogen rich gas stream which is lean in carbon dioxide, and
22 recycling said hydrogen rich gas stream to said reduction
23 reactor.

2. A method according to claim 1, wherein said hydrogen rich gas stream has substantially no carbon dioxide and has significantly less nitrogen relative to said second portion.

3. A method according to claim 1, wherein the separation of H_2 from said second portion of said cooled top gas is made in a PSA or a VPSA adsorption unit.

4. A method according to claim 1, wherein the separation of H_2 from said second portion of said cooled top gas is made in a CO_2 chemical absorption unit.

5. A method according to claim 3, wherein said hydrogen rich gas stream has an hydrogen content equal to or higher than 92% in volume.

6. A method according to claim 3, wherein said hydrogen rich gas stream has an hydrogen content equal to or higher than 95% in volume.

7. A method according to claim 5, further comprising producing a reducing gas as the make-up gas in a steam-natural gas reformer; combining said make-up reducing gas with said first portion of said reducing gas; heating the combination of the first portion and the make up gas to a temperature higher than $750^{\circ}C$ and introducing it to said reduction zone.

8. A method according to claim 5, further comprising combining as the make up gas a natural gas stream or another reformable hydrocarbon, with said first portion of said cooled top gas; circulating such combination through a CO_2 -natural gas

5 reformer thereby producing said stream of reducing gas and
6 introducing said stream of reducing gas to said reduction zone.

1 9. A method according to claim 5, further comprising
2 combining as the make up gas a humidified natural gas stream with
3 said cooled top gas stream and heating said combined stream to
4 form said stream of reducing gas stream, whereby the natural gas
5 present in the reducing gas fed to the reduction zone is largely
6 reformed within the reduction zone taking advantage of the
7 catalytic action of the metallic iron within said reduction
8 reactor.

1 10. A method according to claim 7, further comprising
2 injecting an oxygen or air enriched with oxygen stream to the
3 stream of reducing gas prior to its introduction to said reduction
4 reactor.

1 11. A method according to claim 8, further comprising
2 injecting an oxygen or air enriched with oxygen stream to the
3 stream of reducing gas prior to its introduction to said reduction
4 reactor.

1 12. A method according to claim 9, further comprising
2 injecting an oxygen or air enriched with oxygen stream to the
3 stream of reducing gas prior to its introduction to said reduction
4 reactor.

1 13. A method according to claim 10, wherein said
2 oxygen or air enriched with oxygen stream has an oxygen content
3 higher than 30% in volume.

1 14. A method according to claim 11, wherein said
2 oxygen or air enriched with oxygen stream has an oxygen content
3 higher than 30% in volume.

1 15. A method according to claim 12, wherein said
2 oxygen or air enriched with oxygen stream has an oxygen content
3 higher than 30% in volume.

1 16. A method according to claim 5, further comprising
2 combining hydrogen rich gas stream, with said reducing gas stream
3 and introducing said combination to said reduction zone.

1 17. A method according to claim 12, further comprising
2 heating said hydrogen rich gas stream in a separate heater
3 separate from any prior to its introduction to said reduction
4 zone.

1 18. A method according to claim 5, further comprising
2 feeding said hydrogen gas stream to a cooling zone of said
3 reduction reactor.

1 19. A method according to claim 5, further comprising
2 feeding natural gas to a cooling zone of said reduction reactor.

1 20. A method according to claim 7, further comprising
2 feeding natural gas to a cooling zone of said reduction reactor.

1 21. A method according to claim 8, further comprising
2 feeding natural gas to a cooling zone of said reduction reactor.

1 22. A method according to claim 9, further comprising
2 feeding natural gas to a cooling zone of said reduction reactor.

1 23. A method according to claim 10, further comprising
2 feeding natural gas to a cooling zone of said reduction reactor.

1 24. An apparatus for producing prereduced materials,
2 including DRI, with improved reducing gas utilization, comprising:

3 a reduction reactor having a reduction zone with a gas inlet
4 and a gas outlet;

5 a gas cooler in fluid communication with the gas outlet of
6 said reduction zone;

7 a reducing gas heater in fluid communication with the gas
8 inlet of said reduction zone;

9 first pumping device connected to said cooler and to said
10 heater to recycle reducing gas from said gas outlet to said gas
11 inlet;

12 conduit device for diverting a portion of the reducing gas
13 effluent from said gas outlet of said reduction zone to second
14 pumping device;

15 a separating device for producing a hydrogen rich output and
16 a hydrogen lean output with the carbon dioxide content;

17 a conduit device communicating said second pumping device to
18 said separating device; and

19 a conduit device to communicate from said hydrogen rich
20 output of the separating device to between said first pumping
21 device and the gas inlet of said reduction zone.

1 25. An apparatus according to claim 24, wherein said
2 separating device is a chemical absorption unit.

1 26. An apparatus according to claim 24, wherein said
2 separating device is a physical adsorption PSA or VPSA unit.

120194-4220A (124784A U.S.)

ABSTRACT OF THE INVENTION

A method and apparatus for producing DRI, prereduced materials, or the like, utilized in the steelmaking industry, where hydrogen contained in the gas stream purged from the
5 reduction reactor is separated (preferably by means of a PSA system) and recycled to said reduction reactor. The productivity of the reduction plant is increased by using the separated hydrogen as a chemical reductant in the reactor, instead of using it as fuel. This is particularly useful in upgrading existing DRI
10 production plants.

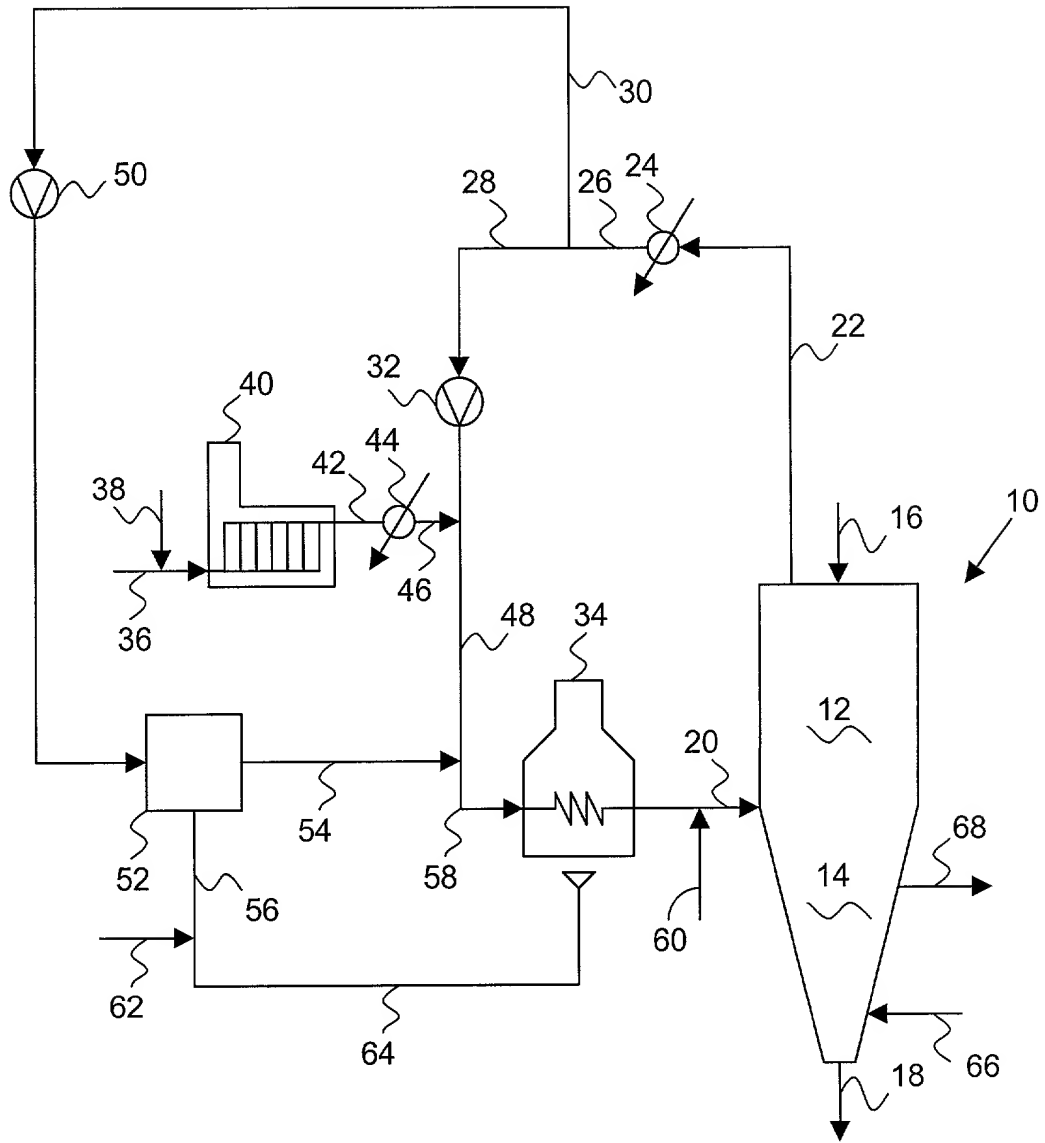


Figure 1

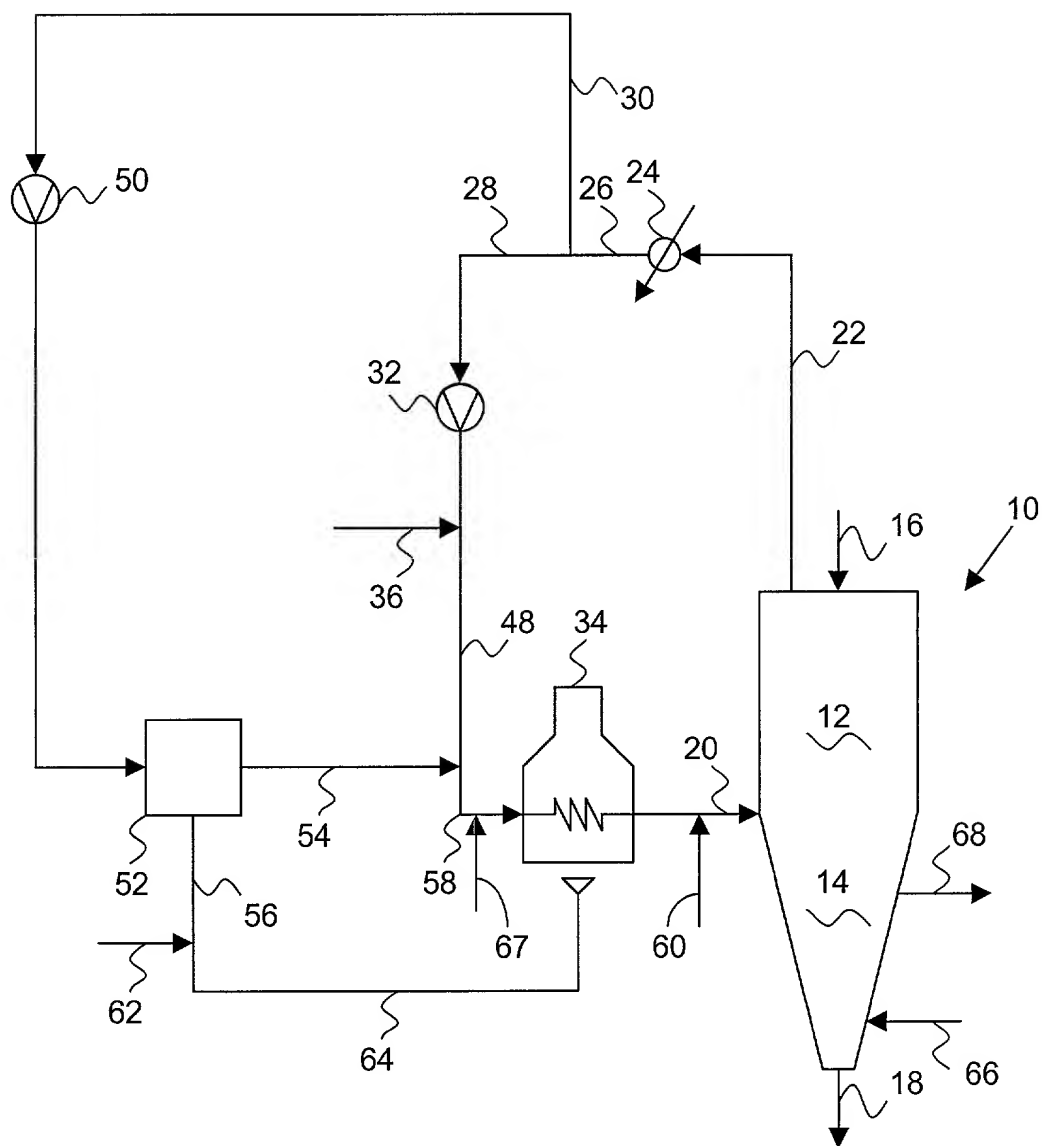


Figure 2

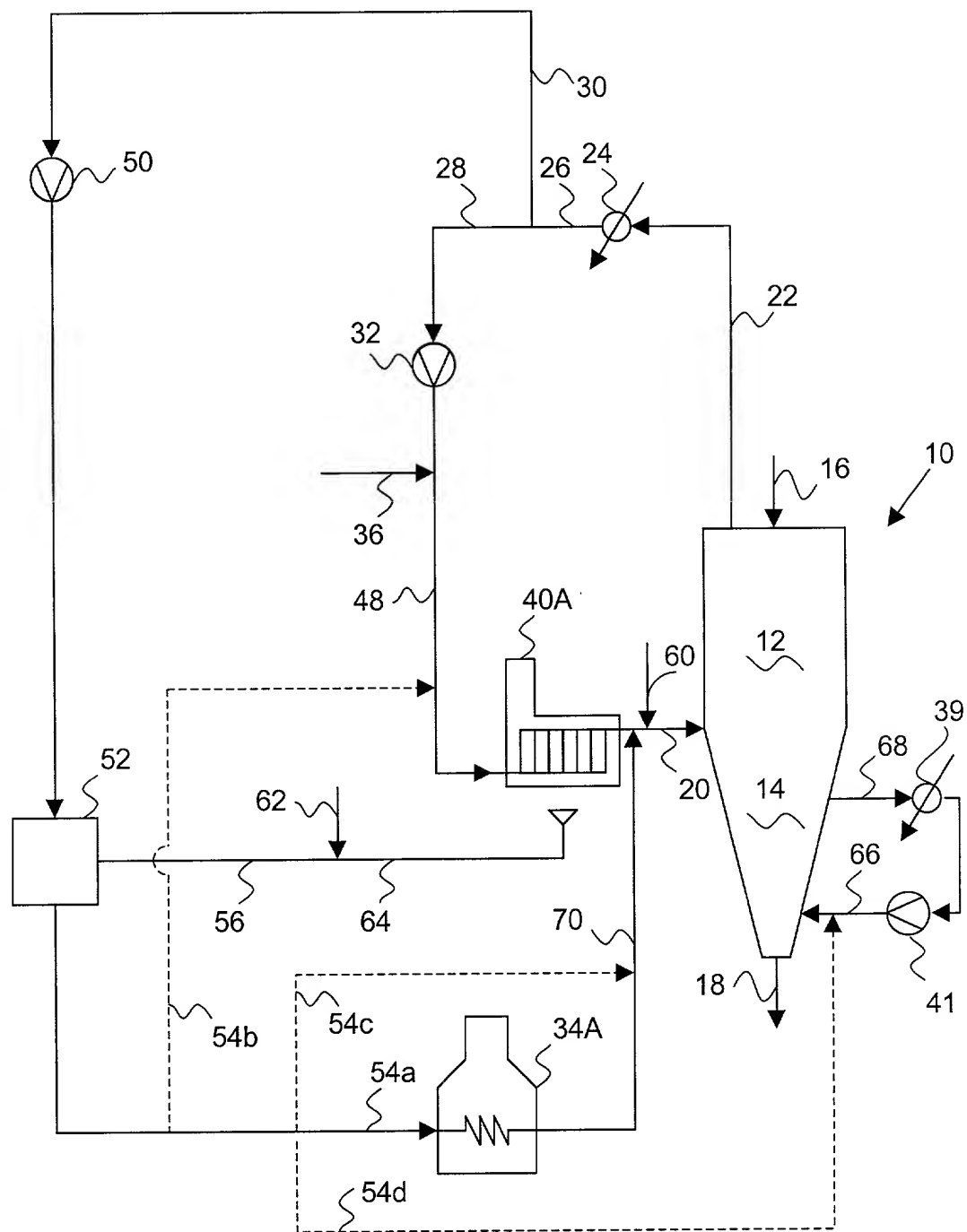


Figure 3

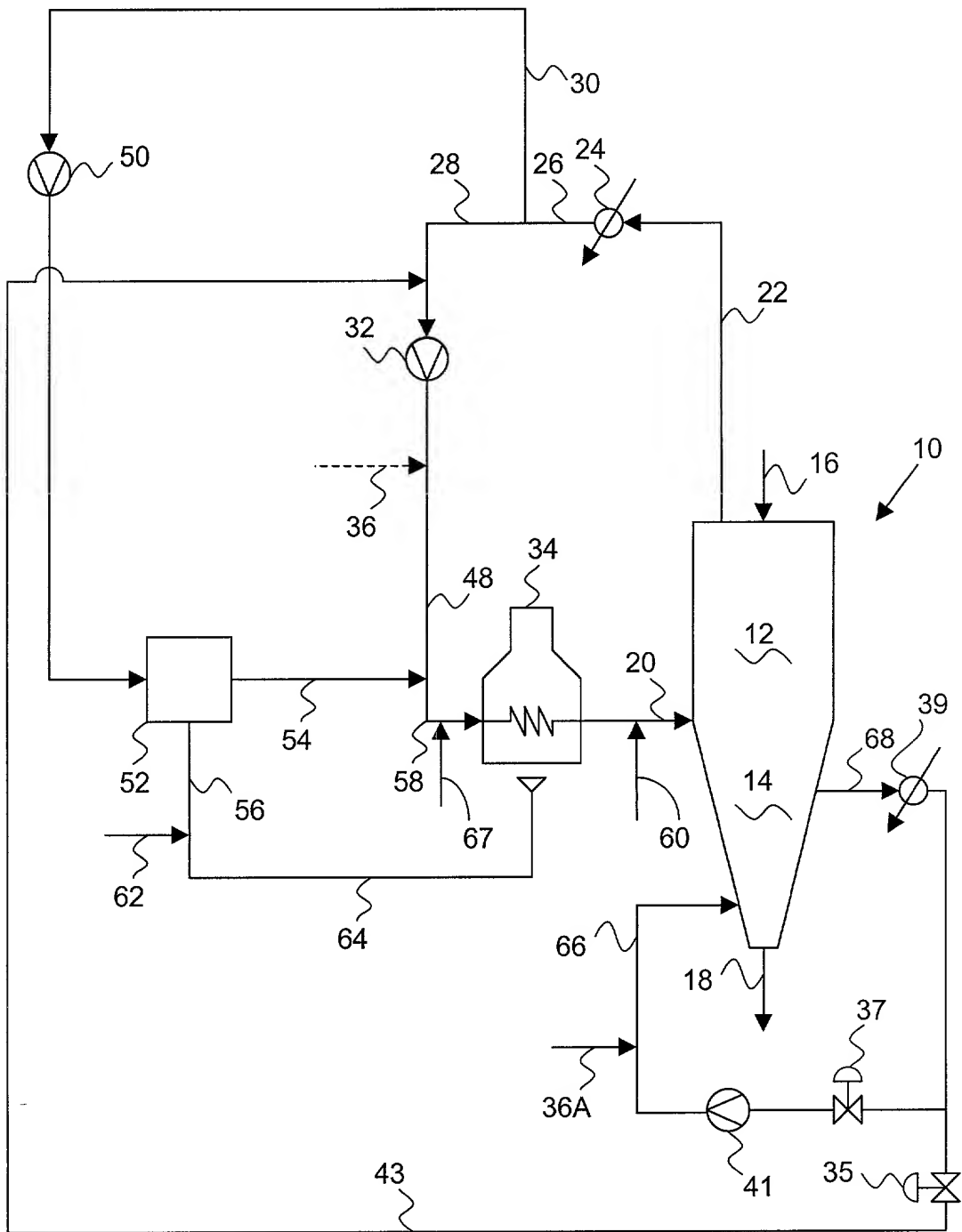


Figure 4

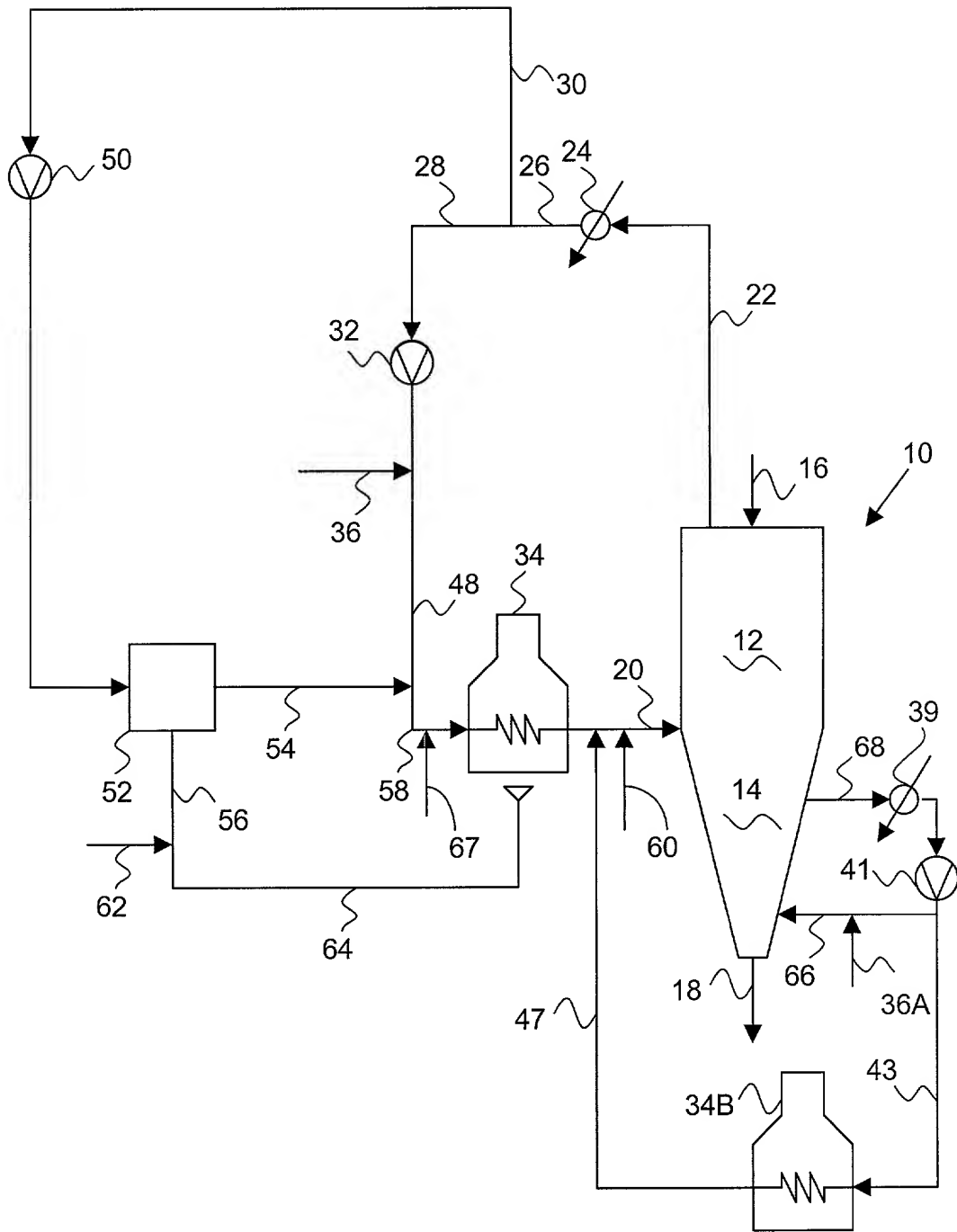


Figure 5

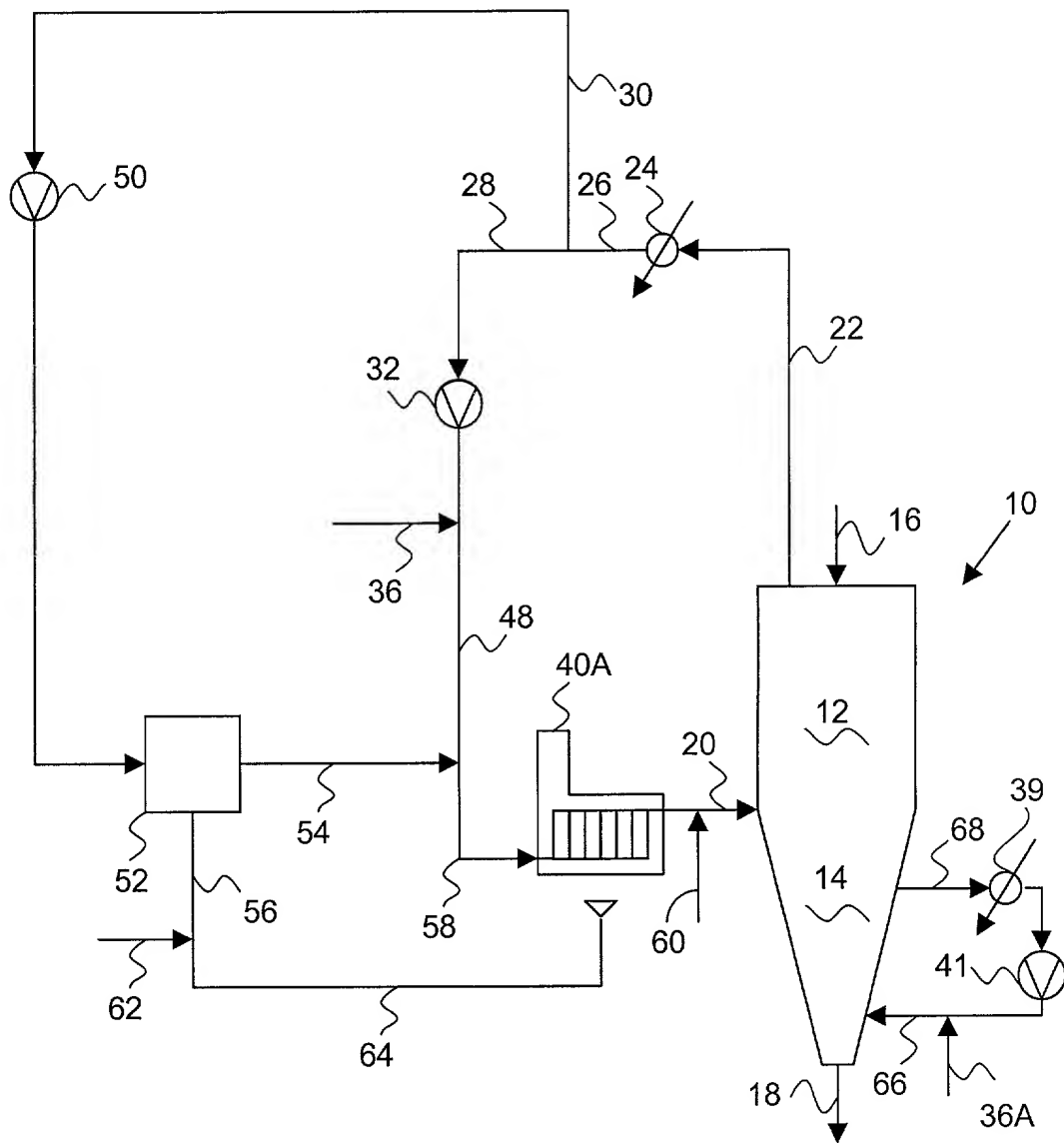


Figure 6

DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

(Under 37 CFR § 1.63)

FROMMER LAWRENCE & HAUG LLP 120194-4220A (124784A U.S.)

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention **ENTITLED:**
METHOD AND APPARATUS FOR PRODUCING DIRECT REDUCED IRON WITH IMPROVED REDUCING GAS UTILIZATION
the specification of which:

 is attached hereto

 X was filed on February 18, 1999 as United States national Application No.
with amendment(s) through (if applicable, give details).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

Prior Foreign/PCT Application(s)

Priority Claimed:

Country (or PCT): Appln. No.: Filed (Day/Month/Year): Yes No

-NONE-

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

Prior U.S. (or U.S.-designating PCT) Applications [list additional applications on separate page]:

U.S. Ser. No.: Filed (Day/Month/Year): PCT Appln. No: Status (patented, pending or abandoned):
60/075,313 02/20/98 **pending**

I hereby appoint A. Thomas S. Safford, Registration No. 21,002, Edgar H. Haug, Registration No. 29,309, and FROMMER LAWRENCE & HAUG LLP, or their duly appointed associate, my attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to file continuation and divisional applications thereof, to receive the Patent, and to transact all business in the Patent and Trademark Office and in the Courts in connection therewith, and specify that all communications about the application are to be directed to the following correspondence address:

A. Thomas S. Safford, Esq.

c/o FROMMER LAWRENCE & HAUG LLP
745 Fifth Avenue
New York, New York 10151

Direct all telephone calls to: (212) 588-0800
to the attention of **A. Thomas S. Safford**

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United

DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (cont'd)
(Under 37 CFR § 1.63)
FROMMER LAWRENCE & HAUG File No. 120194-4280B (124788B U.S.)

States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

INVENTOR(S) :

Signature: _____ Date: February, 1999

Full name of first inventor: **Juan A. Villarreal-Trevino**

Residence: **Alfredo B. Nobel 1994**
Contry Sol, 3° Sector
Guadalupe, N.L. Mexico

Citizenship: **Mexican**

Signature: _____ Date: _____

Full name of 2nd joint inventor (if any):

Residence:

Citizenship:

Signature: _____ Date: _____

Full name of 3rd joint inventor (if any):

Residence:

Citizenship:

Post Office Address(es) of inventors:

Juan A. Villarreal-Trevino
Alfredo B. Nobel 1994
Contry Sol, 3° Sector
Guadalupe, N.L. Mexico

NOTE: In order to qualify for reduced fees available to Small Entities, each inventor and any other individual or entity having rights to the invention must also sign an appropriate separate "Verified Statement (Declaration) Claiming [or Supporting a Claim by Another for] Small Entity Status" form [e.g. for Independent Inventor, Small Business Concern, Nonprofit Organization, Individual Non-Inventor].